THE HARDENING PROPERTIES OF DESULPHURIZATION WASTES

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Abstract

The quality of desulphurization wastes from Finland's coal-fired plants were studied. Laboratory tests were performed on different mixtures of products of the wet-dry method, fluidized-bed reactor and injection technique. The properties under consideration were setting, strength development, permeability and microstructure. Hardening of the waste products were activated with Portland cement and blast furnace slag. Also studied were the utilization alternatives in well compacted concrete.

The hardening properties of the by-products were found to be moderate. The water requirement of products from the injection process and from the fluid-bed process was low. Volume instability was observed in hardened samples made of the products of the wet-dry method without fly ash.

Key-words

Desulphurization, by-products, hardening, permeability.

1. INTRODUCTION

In coal-fired power plants in Finland fly ash is produced annually about 0.4 Mt. During the last years a great deal of fly ash has been utilized in building technology. In the desulphurization process of coal-fired plants solid products are formed. These are sulphite rich products of the wet-dry process and ashes produced by fluid-bed and injection techniques, and gypsum produced in the wet process. Potential objects of utilization are primarily soil construction works and building material industries. In the Technical Research Centre of Finland amounts, quality and utilization of desulphurization wastes were surveyed. Should the consumption of coal increase as expected (to be 6 -8 Mt/a), the amount of desulphurization wastes would be 0.8 - 1.1 Mt/a and the amount of ash would be 0.6-1.0 Mt/a /1/.

In injection method the fine ground limestone is injected in the fire pot, whereat the calcination and reaction with sulphur dioxide take place. In the second reactor the unreacted alkalies can be activated with water, when extra sulphur dioxide is absorbed. In wet-dry method limemilk is sprayed into the fume gases in a separate reactor. The reactor can be situated behind the particle separator, when the content of fly ash in by-product can be regulated. In the fluid-bed method limestone is either bed material or it is fed into the fire place /1/.

The hardening properties of desulphurization wastes from coal-fired plants were studied /2/. The properties under consideration were setting, strength development, permeability and microstructure. Laboratory tests were performed with different mixtures of the products of the wet-dry method, fluidized-bed reactors and injection technique. The hardening of the waste products was activated with Portland cement and blast furnace slag. The utilization alternatives in well compacted concrete products were studied in addition.

2. EXPERIMENTAL STUDY

2.1 Chemical composition and physical properties

The chemical compositions of the desulphurization wastes studied are presented in Table 1.

The total coal content of the Kerava by-product was extremely high. The grain size distribution of the by-products was studied by means of a grain analyzator based on X-ray sedimentation method (Fig. 1). The wet-dry product from Salmisaari (including no fly ash) was remarkably finer than fly ash. The by-products of the fluidized bed method in Kerava (including fly ash) and the product of the injection type method in Inkoo (also including fly ash) were a little finer than mere fly ash.

The grain shape was studied by means of SEM. While fly ash mainly contains smooth and spheric particles, the grain shape of the by-products was more angular (Figs. 2-5). Especially the rest product of wet-dry method including no fly ash was very fine and angular. The density of the by-products studied was measured by Helium pycnometer (Table 2). The density value of the fluid-bed product was higher than that of fly ash indicating that cracking and filling of the hollow spheric particles might occur in the fluid-bed process.

Table 1. The chemical composition of the desulphurization wastes.

Plant	Salmi-saari	Salmi-saari	Kerava	Inkoo
Product / Component	Fly ash	Desulph. product	Fluid-bed product	Injection product
CaO (tot)*	3,6	38	11	15
$CaSO_4$ x 2 H_2O	-	18	17	12
$CaSO_3$ x 0,5 H_2O	-	60	<5	<5
$CaCl_2$ x 4 H_2O	-	8,4	0,08	0,8
CaO **	-	3,4	5,0	5,6
SiO_2	51	2,0	37	42
Al_2O_3	14	0,9	19	22
Fe_2O_3	7,6	0,5	5,0	7,7
K_2O	2,1	0,05	0,9	1,9
Na_2O	1,1	2,0	0,6	5,5
MgO	1,7	-	1,4	3,0
TiO_2	-	-	0,7	0,8
Cl		3,3	0,03	0,3
S (tot)		18,2	3,2	2,3
C (tot)			19	2,2
N (tot)		0,19	0,25	0,2

* assuming that all the calcium content exists in oxide.
** assuming that all the calcium not bound in sulphate, sulphite, carbonate and chloride exists in oxide.

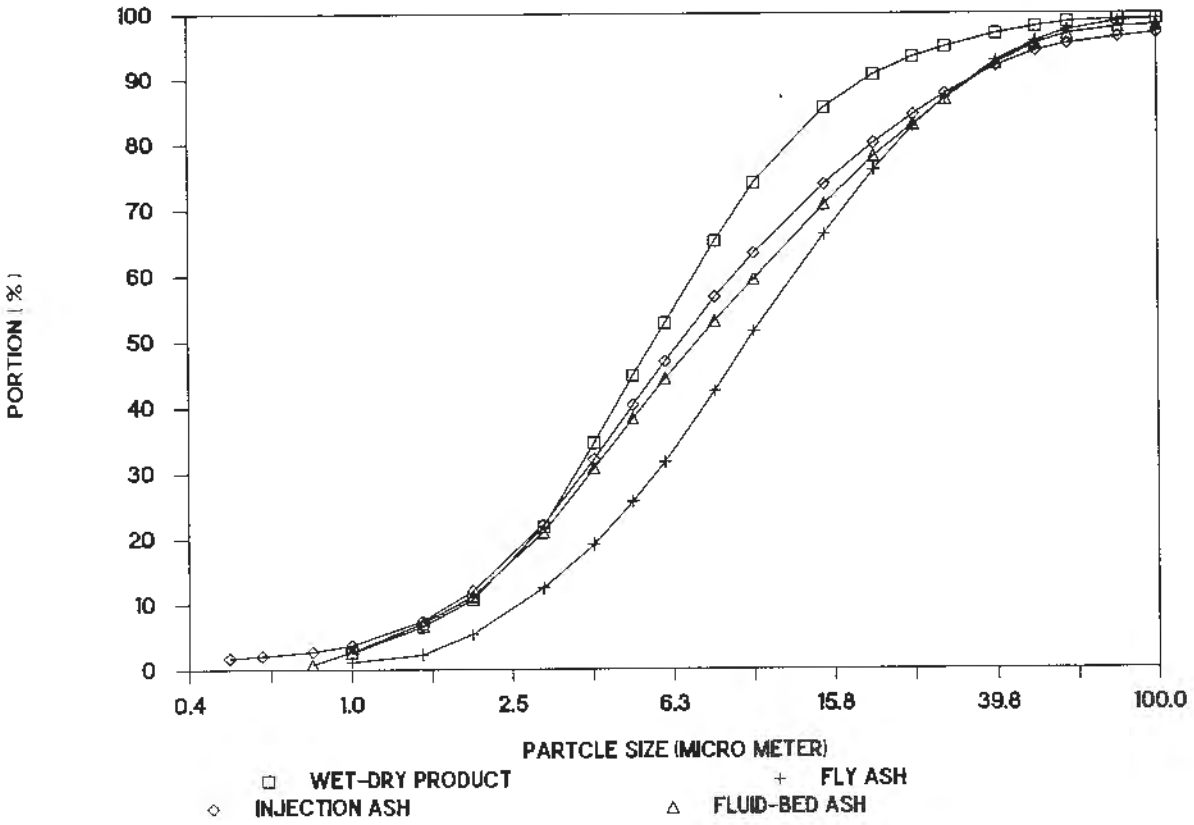

Fig. 1. The grain size distribution of the desulphurization products

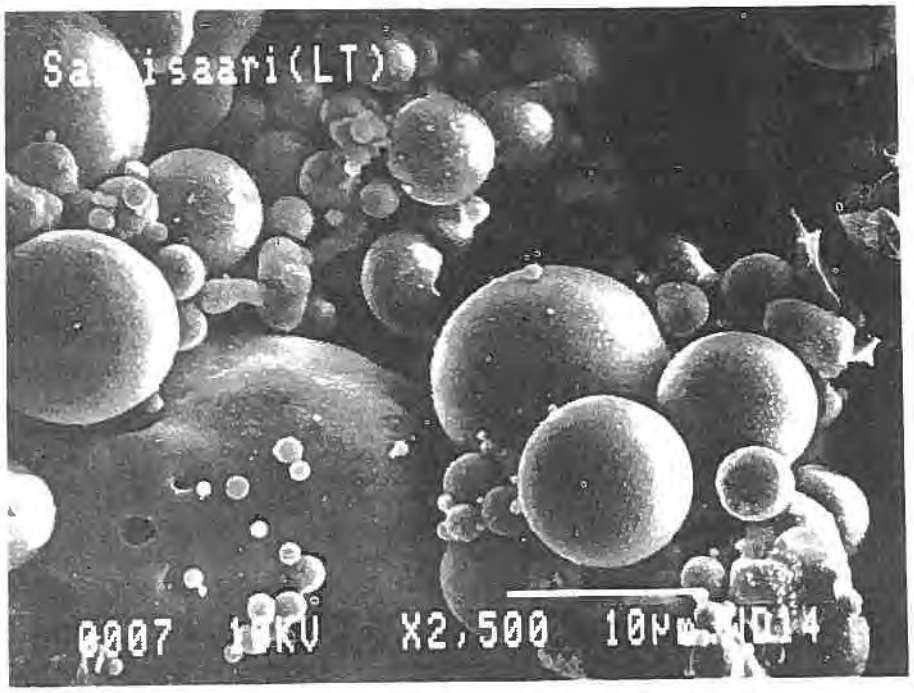

Fig. 2. Fly ash from Salmisaari coal-fired power plant. Scanning electron microscope photograph. Magnification 2500.

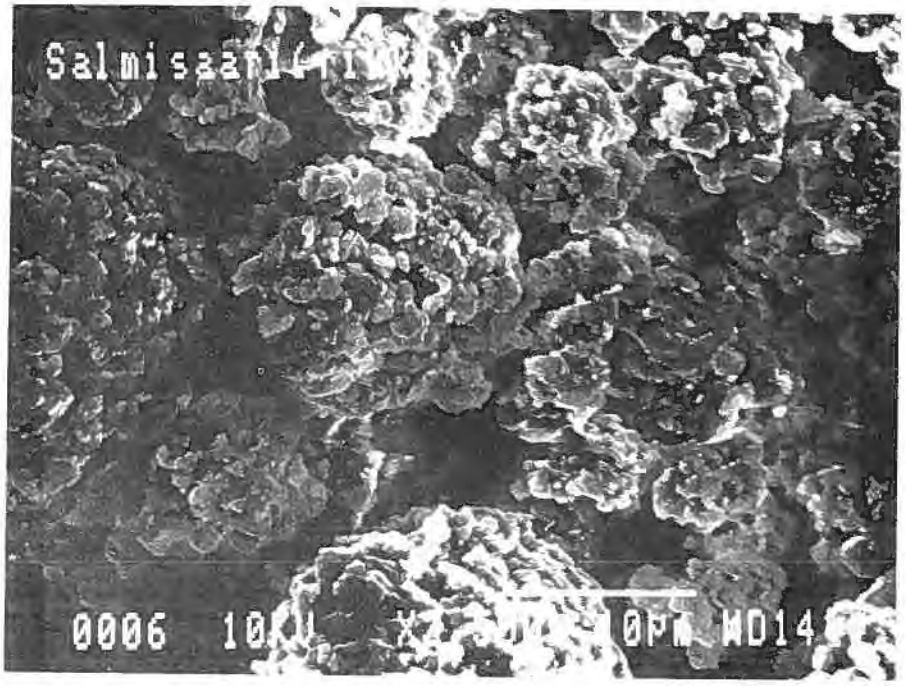

Fig. 3. Desulphurization product from wet-dry method. Scanning electron microscope photograph. Magnification 2500.

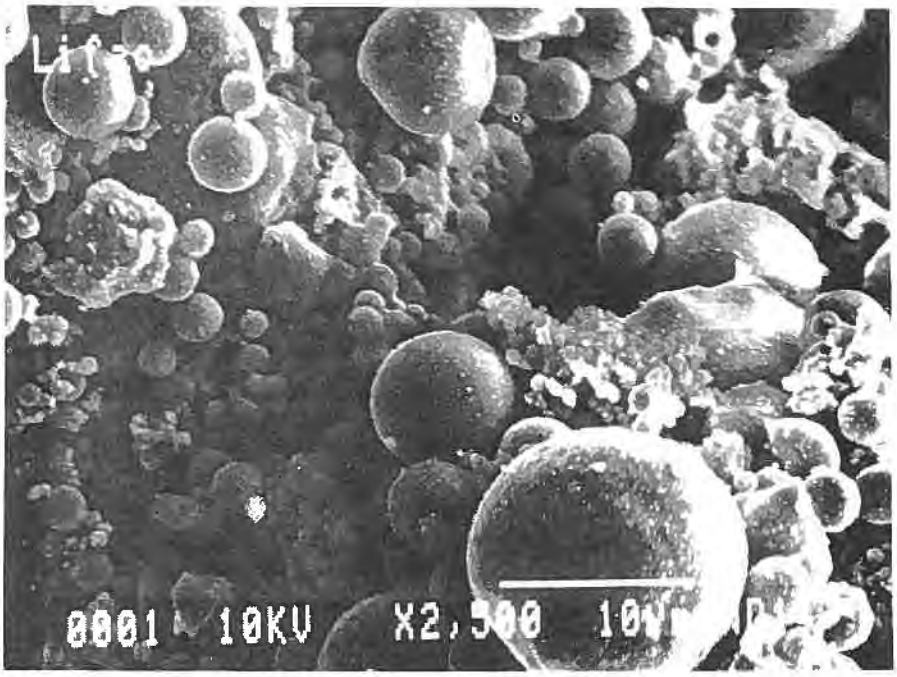

Fig. 4. Desulphurization product from injection method. Scanning electron microscope photograph. Magnification 2500.

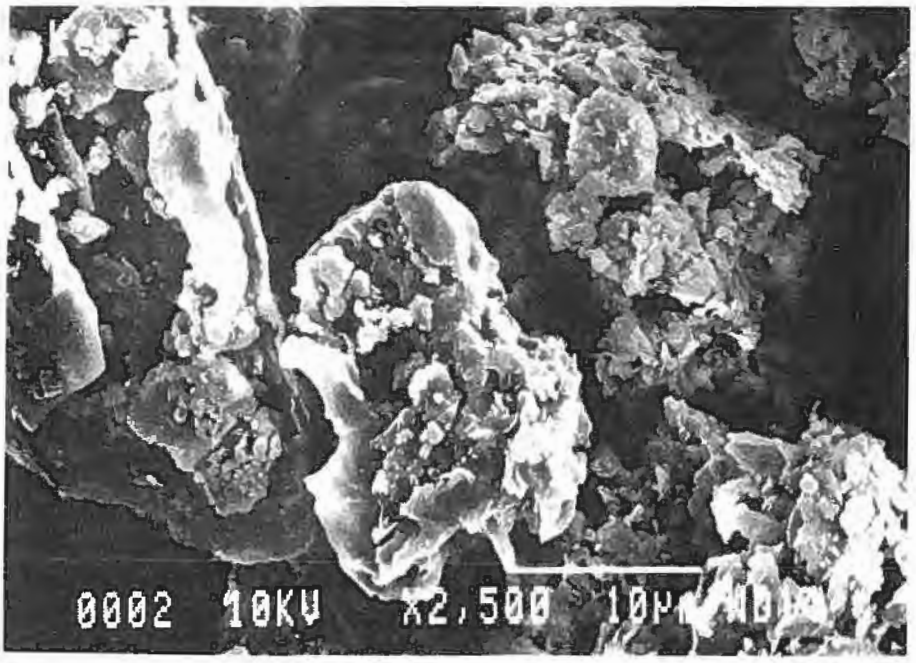

Fig. 5. Desulphurization product from fluidized bed process. Scanning electron microscope photograph. Magnification 2500.

Table 2. Density of the by-products.

	Density kg/m^3
Fly ash (Salmisaari)	2,25
Wet-dry product (Salmisaari)	2,35
Fluidized bed product (Kerava)	2,99
Injection by-product (Inkoo)	2,49

2.2 Water requirement

The effect of the quality of the desulphurization waste on the water requirement of the paste was studied by means of Haegerman equipment (DIN 18555) (Table 3). The water requirement of the by-product from the injection method and that of the fly ash were of the same order, but the water requirements of the wet-dry product and the fluid-bed product were remarkably higher than the water requirement of fly ash. The high water demand of the paste made of fluid-bed product resulted obviously from the high coal content and the lack of the sphere shaped particles and that of the paste made of wet-dry product resulted from the fine grain composition and the angular shaped particles.

Table 3. The spread value of the paste.
The composition of the binding material:
60% desulphurization by-product
30% blast furnace slag
10% Portland cement P40/7.

	Spread value, cm			
By-product	Water-binder ratio 0,31	0,37	0,43	0,50
Fly ash	15,0	22,0	25,0	-
Wet-dry product	*	12,5	13,5	16,0
Fluid-bed product	*	11,5	14,0	-
Injection product	17,0	23,0	25,0	-

* The paste could not be cast with such a low water-binder ratio.

2.3 The hardening properties of the paste specimens made by desulphurization products

The paste samples were made of water and the binding material. The specimen size was 40 x 40 x 160 mm^3. The specimens were cured at 20°C and in the relative humidity of 95%. The binder compositions studied are presented in Table 4. The effect of the binder composition, age, water cement ratio and curing conditions on the strength development were studied. The results are presented in Figures 6 - 11.

Table 4. The composition of the binding material.

	Composition
Mixture 1	60% desulphurization by-product 40% blast furnace slag
Mixture 2	60% desulphurization by-product 30% blast furnace slag 10% rapid hardening Portland cement
Mixture 3	60% desulphurization by-product 40% rapid hardening Portland cement

According to the results the fluidized bed product from Kerava hardened significantly better with Portland cement than with blast furnace slag, but the by-product from wet-dry process hardened in the best way with ground granulated slag. When the strength is evaluated on the basis of the strength value at the age of four weeks one can see that the by-product from injection

process hardened as well with Portland cement as with blast furnace slag. The highest final strength values were observed in samples made of injection product, but the highest early strength values were observed in the paste samples made of the fluid-bed product. Wet curing conditions were advantageous on the strength development of the products from the wet-dry process and from the injection process.

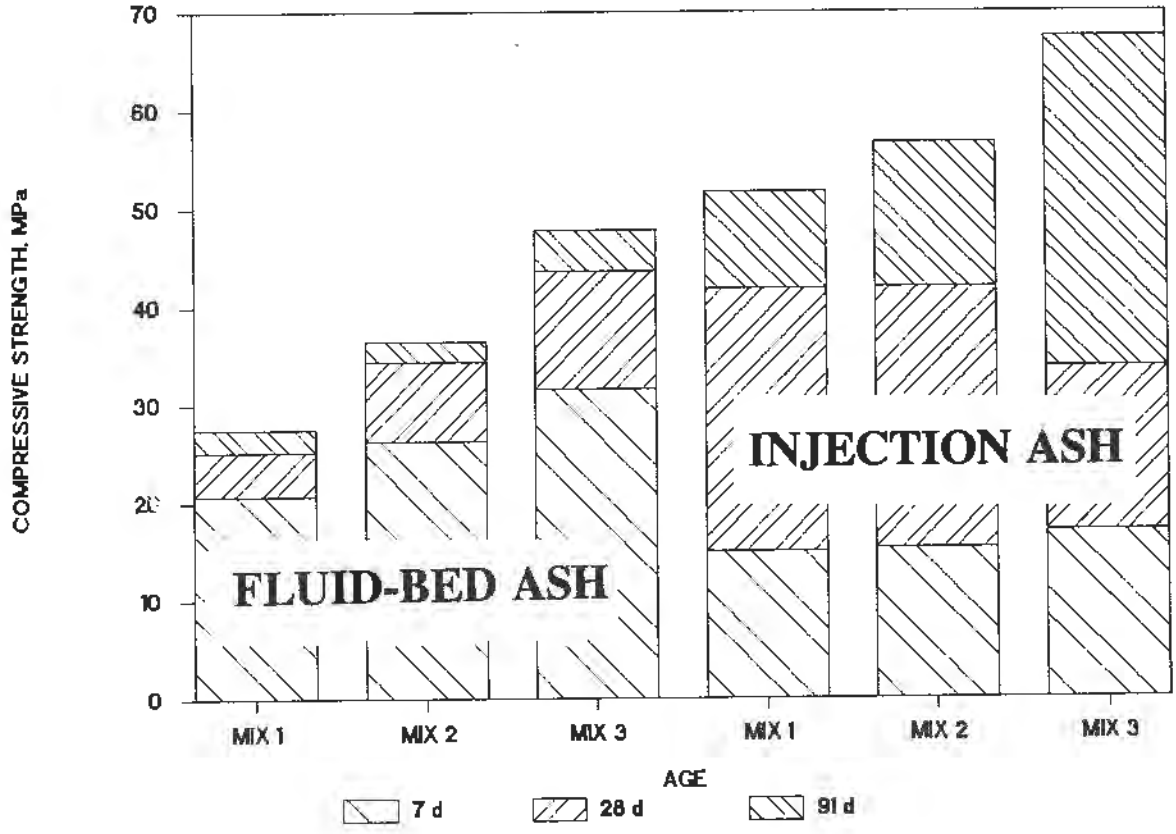

Fig. 6. The effect of the composition of the binding material on the compressive strength of the paste.
Mixtures 1 - 3 (Table 4).
Water-binder ratio 0,37.
Desulphurization products from the injection process and from the fluidized bed method.

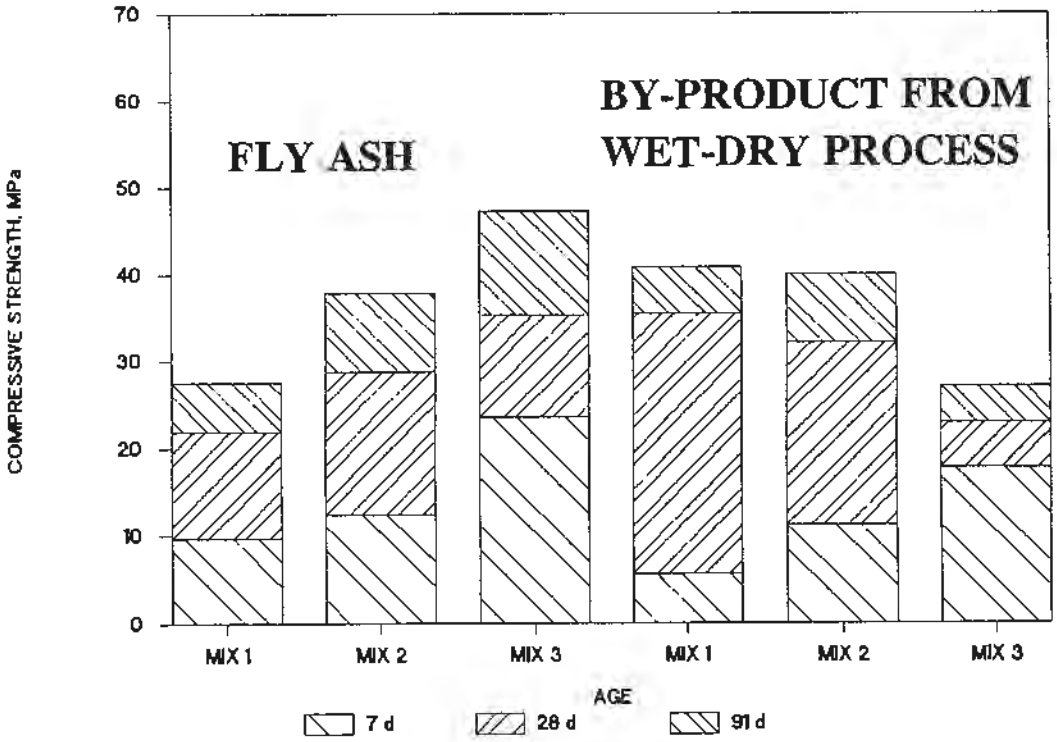

Fig. 7. The effect of the composition of the binding material on the compressive strength of the paste. Mixtures 1 - 3 (Table 4). Water-binder ratio 0,37. Fly ash and the desulphurization products from the wet-dry method.

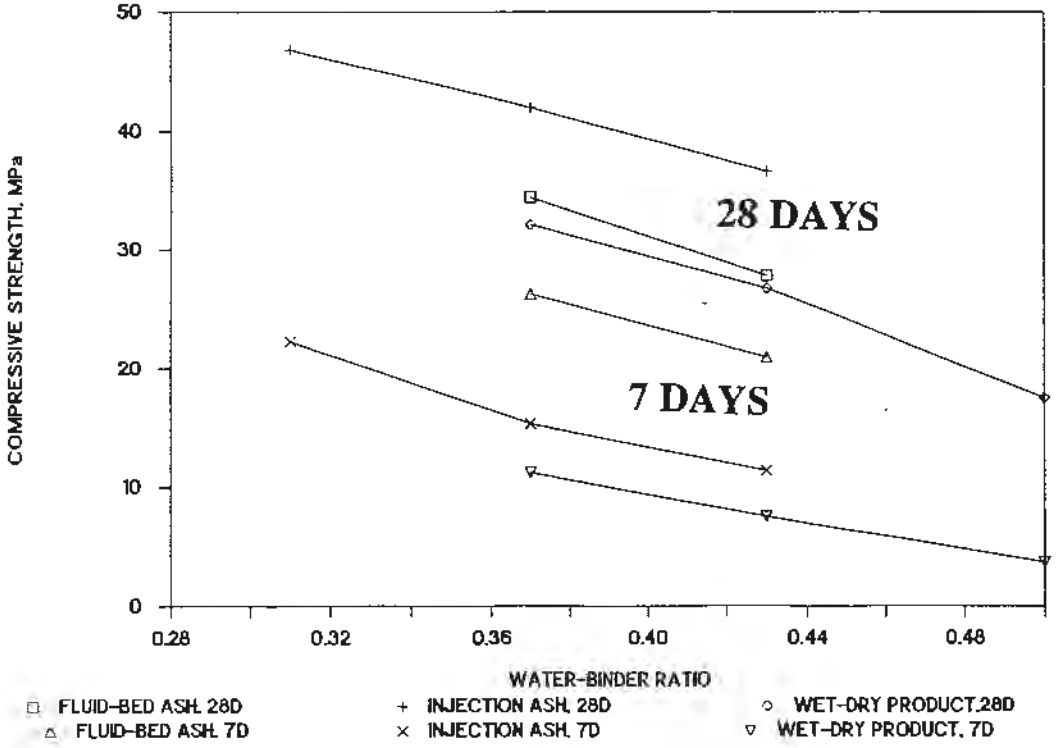

Fig. 8. The effect of the water binder ratio on the compressive strength at the ages of 7 and 28 days. Binder mixture 2 (Table 4).

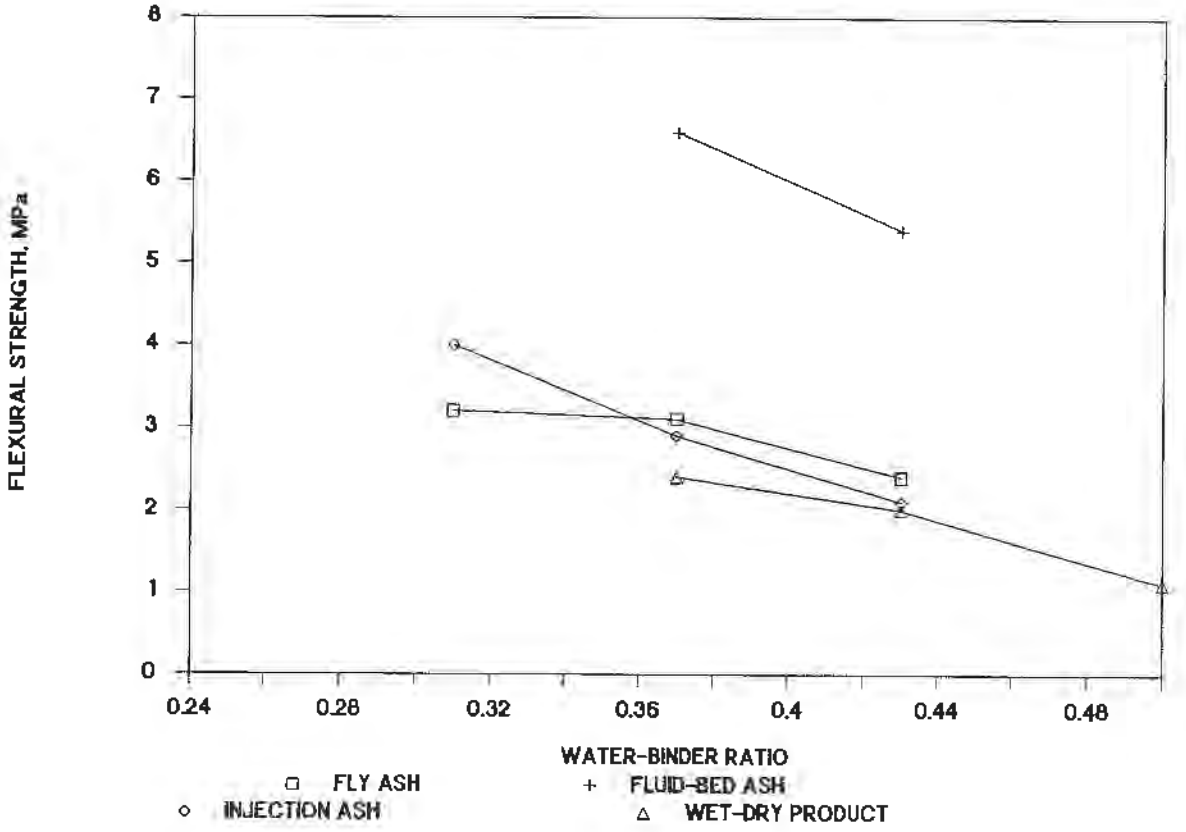

Fig. 9. The effect of the water binder ratio on the bending strength at the age of 7 days. Mixture 2 (Table 4).

The paste samples were studied by means of optical microscopes in the age of three months. Petrografic thin sections impregnated by fluorescent resin were prepared. In the samples made of fluid-bed product activated with cement or slag there existed only few cracks but the amount of air pores was considerable. The pores resulted probably from the gas production which occurred when the desulphurization ash was mixed with water. In the wet cured samples there existed a few more cracks than in the samples cured at 70% relative humidity. No crystallizations were observed.

In the paste samples made of the by-product of the injection process there existed more micro cracks but less air pores than in the samples made of fluid-bed product. In all the samples the amount of cracks was little, but most of all there existed micro cracks in the samples made of the mixture of the by-product and blast furnace slag. In the wet cured samples more cracks were observed than in the samples cured at the 70% relative humidity. No crystallizations were observed.

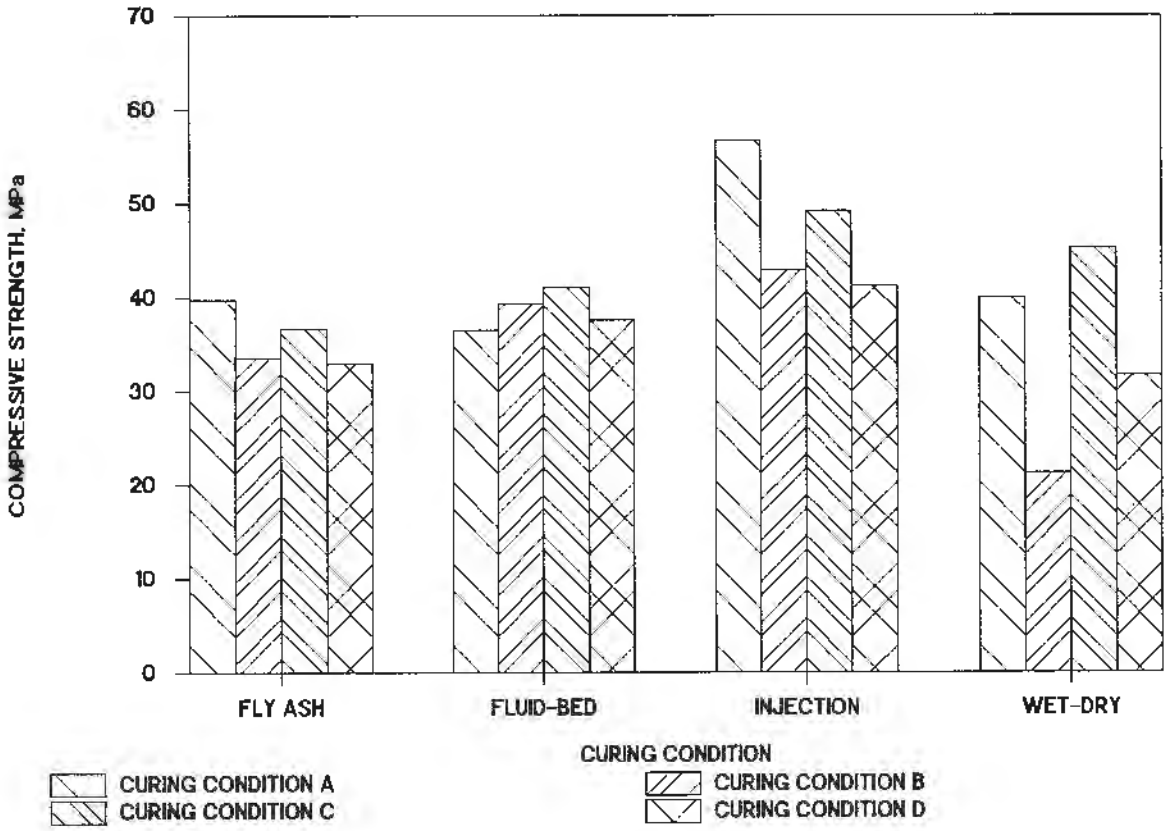

Fig. 10. The effect of the curing conditions on the compressive strength of the paste specimens. Water binder ratio 0,37. Binder mixture 2 (Table 4). Curing conditions:

A	91 d RH > 95%.	B	7 d RH > 95%
C	7 d RH > 95%		84 d RH = 70%.
	21 d RH = 70%	D	7 d RH > 95%
	14 d in water		35 d RH = 70%
	7d oven at 50°C.		7d drying at 50°C.

2.4 The micro structure and the volume stability of the paste samples

Paste samples were cured further on for two years at the temperature of 20°C and in the 95% relative humidity. The compositions of the binding materials are presented in Table 4. During the two years' curing the specimens made of the by-product of the wet-dry process and Portland cement (mixture 3) were totally cracked and there appeared cracks in the corners of the specimens made of the by-product of the wet-dry method and blast furnace slag (mixture 2). The samples were studied by means of scanning electron microscope. Considerable crystallizations were noticed. According to the results of the X-ray study plenty of ettringite existed in both samples, but in the sample made of the mixture 2 there were more ettringite than in the sample made of the mixture 3. In addition in the sample made of the by-product and Portland cement (mixture 3) also gypsum was observed. The amount of gypsum was approximately as high as the amount of ettringite. Gypsum was not noticed in the samples made of the by-product and blast-furnace slag (mixture

2). In addition a plenty of calcium sulphite ($CaSO_3$ x 0,5 H_2O) appeared in both samples.

Long time volume instability was not observed in the specimens made of the desulphurization products of the fluidized-bed reactors and the injection technique.

2.5 Hardening without an activator

The hardening of the by-products without other components was studied in such a way that the specimens were prepared with an Intensive Compactive Tester. The apparatus compacts the fresh paste by means of shear compacting. During the test the sample is in a working cylinder and the density of the sample can be observed. The compaction conditions are very similar to those that occur in practice by the casting of no slump concrete by the extruder machines.

The water content of the mixture was as small as possible. The strength results are presented in Table 5. According to the results the by-product from the injection technique hardened moderately without other binder components.

Table 5. The compression strength of the specimens compacted by means of Intensive Compactive Tester. Cylinder size: diameter 100 mm, height 100 mm.

Binder. By-product from	Water binder ratio	Compressive strength MPa	Age d	Density of the green sample kg/m^3
wet-dry method	0,46	0,56	28	1380
fluid-bed method	0,46	1,31 2,57 3,85	7 28 91	1699
injection method	0,23	2,69 18,5 31,2	7 28 91	1983

2.6 Well compacted concrete specimens

Well compacted concrete specimens were prepared of the by-products. Specimens were either beams (100 x 100 x 500 mm), which were compacted on the vibrating table by compressive pressure, or cylinders (100 x ϕ100 mm), which were compacted by

means of Intensive Compactive Tester. The binder content of concrete was 400 kg/m^3. In some concrete mixtures also the finest content of the aggregate (6% by weight) was substituted by the by-product. The water content was as small as possible. The composition of the binder, water binder ratio and the density value of green concrete achieved by means of intensive compacting are presented in Table 6.

Petrografic thin sections impregnated with fluorescent resin were prepared of the concrete cylinder samples number 1 and 3 (Table 6) at the age of four months. The thin sections were studied by means of optical microscopes. In the concrete sample made of fluid-bed product there were quite a lot of air pores and a few micro cracks in the boundary layer between the aggregate particles and the paste. In the concrete sample made of injection by-product the hardened paste was very dense but there appeared few micro cracks in the boundary layers. No gypsum, ettringite or other crystallizations were observed in either of the concrete samples.

Table 6. The composition of the binder, water binder ratio and the density of green concrete.

Concrete	Binder	Water binder ratio	Density kg/m^3
1	40% P40/7 (1 60% FBP (2	0,4	2330
2	40% P40/7 (1 60% FBP (2 no filler	0,3	2160
3	40% P40/7 (1 60% IP (3	0,3	2522
4	40% P40/7 (1 60% IP (3 no filler	0,3	2467
5	40% P40/7 (1 60% WDP (4 no filler	0,65	-

1) Rapid hardening Portland cement
2) Fluid-bed product
3) Injection product
4) Wet-dry product

The strength results are presented in Table 7. According to the results short curing time did not significantly decrease the strength development of the concrete made of fluid-bed rest product. The lowered curing temperature decreased remarkably the strength value of the concrete made of fluid-bed product, while the strength of the injection product concrete did hardly decrease.

Table 7. The strength of the well compacted concrete specimens.

Table 7. The strength of the well compacted concrete specimens.

Concrete beams. Age and curing	Compressive strength MPa Concrete (Table 6) 1	2	3	4	5
7 d RH>95% T 20°C	5,5	1,9	19,6		
28 d RH>95% T 20°C	12,4	3,4	37,8		
3d RH>95% T 20°C	12,1				
28 d RH>95% T 10°C	6,6		31,1		
Concrete beams. Age and curing	Flexural strength MPa Concrete (Table 6) 1	2	3	4	5
7 d RH>95% T 20°C	1,3	0,4	2,5		
28 d RH>95% T 20°C	2,1	0,8	3,6		
3d RH>95% T 20°C	1,9				
28 d RH>95% T 10°C	1,3				
Cylinders. Age and curing	Compressive strength MPa Concrete (Table 6) 1	2	3	4	5
7 d RH>95% T 20°C				38,8	
28 d RH>95% T 20°C	45,9	19,3	65,0	43,5	16,9

The frost resistance of the well compacted concrete specimens was tested. The temperature varied between +20°C and -20°C. The concrete specimens were frozen in air and they thawed in water. The duration of one cycle was about 8 hours. The weight of the specimens was recorded during the first 200 cycles, but the weight did not decrease. The durability of the surfaces of the concrete samples was good, but one of the beams made of fluid-bed product was broken. The compressive strength of the cylinders after 600 - 800 frost cycles was about the same as in the age of four weeks. The average strength of the beams made of fluid-bed product decreased, but the strength of the specimens made of the injection product did not decrease under

the frost test. The frost resistance of the specimens made of the by-products seemed to be better the more complete was the compacting of the fresh concrete.

In order to test the capillary suction of the well compacted specimens the samples were dried (T=+50°C), whereafter the samples were placed on a grid so that the lower surface of the sample came into contact with water. The increase of the weight was recorded during two weeks. After that the specimens were saturated with water by means of water pressure (15 MPa) and cured in water in order to measure the total porosity. In the end of the test the specimens were dried at the temperature of 105°C in order to find out the dry weight of the samples.

According to the capillary suction results (Table 8) the concrete mixtures 1 and 3 (Table 6) were very well compacted. The capillary suction of the specimens was extremely low. The air pore content in the samples made of the fluid-bed product resulted in high total porosity. The air pores get slowly filled and so the resistance value of the concrete number 1 (Table 6) is high. According to the porosity results the concrete number 2 made of fluid-bed product was not well compacted. The average total porosity of the samples were high and in addition the permeability was considerably higher than that of the other samples.

Table 8. The results of the capillary water suction test. Samples are sawn from cylinders compacted with intensive compactive tester. Concrete samples were cured at 20°C and in the relative humidity of 95%. The age of the samples was 2 months.

Concrete	Total porosity l/m^3	Capillary index $kg/(m^2 \sqrt{s})$	Resistance s/mm^2
1	164	0,009	42,9
2	219	0,085	3,5
3	137	0,004	35,7

3 DISCUSSION

The physical and hardening properties of the desulphurization by-products and the strength development, durability and the micro structure of the hardening products made of the desulpharization ashes were studied. The by-products taken into the consideration were the products from wet-dry process in Salmisaari, injection type process in Inkoo and fluidized bed process in Kerava.

The most important properties of the by-products seemed to be the coal content of the product, the grain shape of the particles and in addition the sulphite content of the product. The coal content, the grain size distribution and the grain shape of the particles effected strongly the water requirement of the products and on the compacting properties of the paste and concrete made of the products. The sulphite content of the product had an effect on the volume stability of concrete. Those by-products containing mainly smooth and spheric particles had a low water requirement and well compacted specimens with good or moderate strength development and low permeability could be produced. Strong volume instability occurred in hardening products made of the by-product from wet-dry method excluding fly ash. High amounts of crystallizations were observed. On the other hand the hardening products of the desulphurization ashes from the injection type process and the fluidized bed process including fly ash remained stable in volume during the two years' curing.

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